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THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYTICAL INVESTIGATIONS ON SEWAGE FARM SOILS

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Abstract

Soil substrates of sewage farms (inflow of sewage areas) and of closed sewage farms were investigated by means of thermogravimetry and differential thermal analysis. The results were compared with those obtained for control samples from outside the sewage farms.

The organic matter of actively used sewage areas (inflow) contains a remarkable amount of easily oxidizable compounds brought to the inflows by suspended matter.

Beside these compounds, macromolecular organic substances predominate in the composition of the organic matter and are responsible for an immense heat release in the high temperature range of the thermal studies.

In the substrates of closed sewage farm inflows or of other sewage farm areas which do not belong to the inflows, the amounts of volatile and easily oxidizable compounds decrease rapidly. The substrates hardly differ in their reaction temperatures from control samples. The influence of single macromolecules on the exothermic oxidation is reduced with increasing humification.

Keywords: composition, DTA, organic matter, sewage farm soil

Introduction

Up to the present time a remarkable amount of municipal sewage has oozed away through sewage farms.

For almost one century the sewage of the Berlin conurbation was brought to farms in the surroundings of the city. In the Berlin sewage farms the water passes through sewage ponds in which a large amount of the suspended particulate matter becomes sedimented. The ponds have to be cleaned periodically. The water comes to the sewage areas via open supplies (ditches). In the inflow of the areas, suspended particles are again sedimented, like in a river mouth (Fig. 1).

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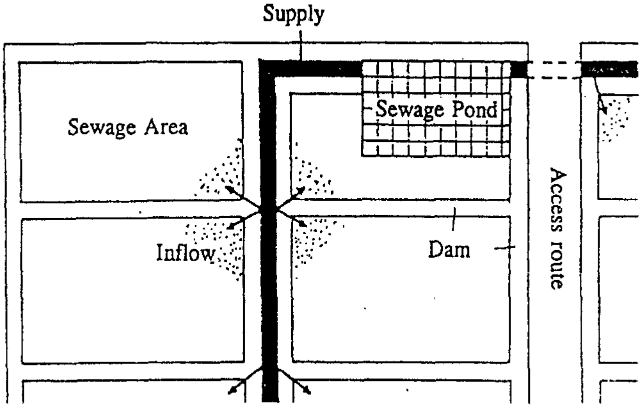

Fig. 1 Sewage farm elements

The particles consist of insoluble organics or of inorganic matter on which organic compounds are adsorbed.

In both cases the particles contribute to the organic matter (OM) of the inflow.

Because of this permanent fertilization and of the periodic flooding, the soils of sewage farms show a high content of OM. The OM is a key parameter which determines other soil properties like total exchangeable bases, bioactivity, humidity and others [2].

Soil pollutants are fixed by adsorption or chemical bond. OM is an important deposit site for sewage pollutants [3].

The cessation of irrigation and the reshaping of the sewage areas resulted in an increased mineralization and in a change of the composition of the OM. This affects the metabolisms and the mobility of the pollutants and their metabolites.

To study the composition of OM in sewage farm soils and structural changes of the OM in closed farms, soil substrates were investigated and compared with control samples. Thermoanalytical studies proved to be suitable for characterization of the composition of OM particularly for the investigation of organo-mineral complexes in sand, silt and clay fractions of soil substrates [6].

The soil substrates can be classified as sand or silty sand.

The samples were not fractionated into silt and sand before the analytical investigations. The results of investigations were used to describe the interaction between OM and mineral substrate as a whole. Only litter was removed by sieving (d=2 mm).

Characterization of the substrates/soil description

The succession of plates and lowlands is typical of the landscape in the south of Berlin.

The investigated sewage farms are situated on the Teltow-plate, a ground moraine covered with sand and formed during the Weichsel glacial period.

Sandy-Cambisols and Luvisol/Podzoluvisols predominate. Their OM content is about 2%. The utilization as sewage farms led to soils which had increasingly artificially disturbed structures [2].

The investigations were performed on substrates of uppersoil samples. The sample locations are described in Table 1.

Experimental methods

The samples were taken from a depth of 0–30 cm and transported in brown jars. In the laboratory, the samples were air-dried, sieved (d=2 mm), ground (DIN 38414/7) and freeze-dried (LYOVAC GT2).

Table 1 Locations of the investigated soil substrates

Location	Name	OM content/%		Bound water/%	Soil type	Utilization
		1	2	1		
Sewage pond	B62	47.62	53.4	5.18	–	–
Sewage field	R11	10.94	11.9	0.59	sand	green fallow
(inflow)	R13	15.71	18.7	1.53	sand	green fallow
Sewage field	F23	5.59	7.1	1.19	sand	green fallow
	F63	2.24	3.4	0.57	silty sand	green fallow
	F12	3.06	3.8	0.43	sand	field irrigation stopped, 4 y. before
	F05	2.96	3.6	0.39	silty sand	field irrigation stopped, 20 y. before
	F08	2.60	3.2	0.37	silty sand	field irrigation stopped, 20 y. before
Control samples	V10	2.98	2.6	0.40	silty sand	field
	V72	1.47	2.0	0.36	sand	green fallow
	V82	1.92	3.1	0.78	sand	woodland
	VZ1	18.94	22.6	3.40	sand	green lowland (moor)
Artificial substrates	K1	1.95*	–	1.88	–	–
Sand/Na-Humate	K2	4.50*	–	2.38	–	–
	K3	19.00*	–	2.92	–	–

*% Na-Humate

1 by thermogravimetry 2 annealing DIN 19684 by thermogravimetry

The amount of OM was measured by means of annealing (DIN 19684/2) and confirmed by thermogravimetry.

Simultaneously thermogravimetric and differential thermal analyses were performed on a thermobalance L81 (Linseis) in vertical operation mode, using platinum crucibles under normal atmosphere. The heating rate was 5 K min^{-1}. The reference material for DTA-measurements was ignited Al_2O_3. For interpretation the special softwares STA (TG measurement) and Linseis (DTA measurement) were used.

Results and discussion

As the samples were freeze-dried, the amount of free water was negligible, as proved by the TG curves (Fig. 2).

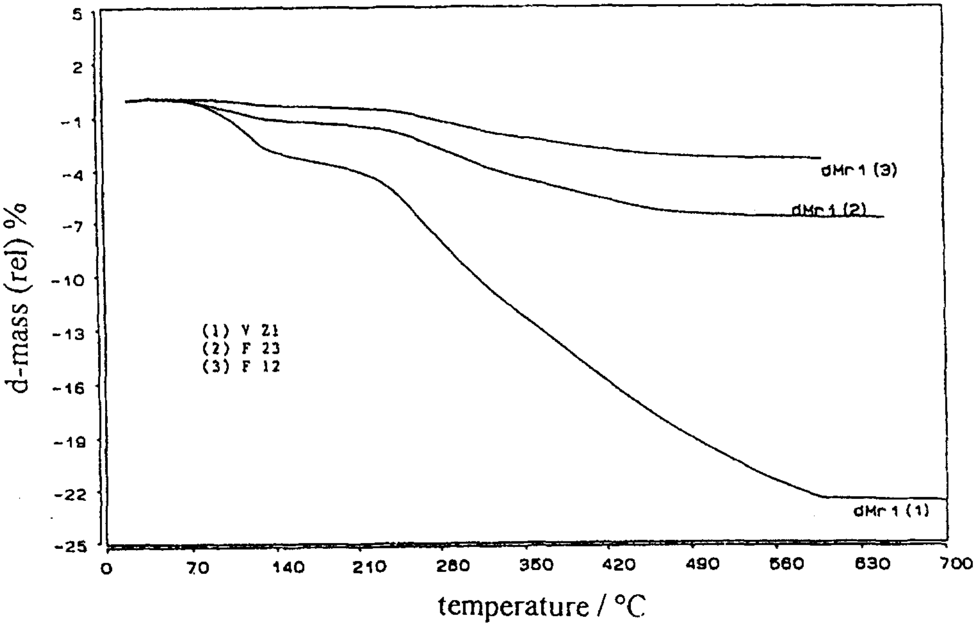

Fig. 2 TG curves of substrates V Z1, F 23, F 12

The corresponding DTA curves show that the first step of mass loss is always an endothermic reaction. Most probably it originates from the dehydration of bound water. The amount of bound water increases with increasing OM content (Table 1). The water bound by OM is released up to 160°C. This can be seen in Fig. 3, showing the TG and DTG curves of sample VZ1 with high OM and bound water content (Fig. 3).

Mass losses above 180°C are mainly connected with exothermic reactions due to combustion of the OM. The total mass loss in the TG plots corresponds to the values obtained by annealing (Table 1).

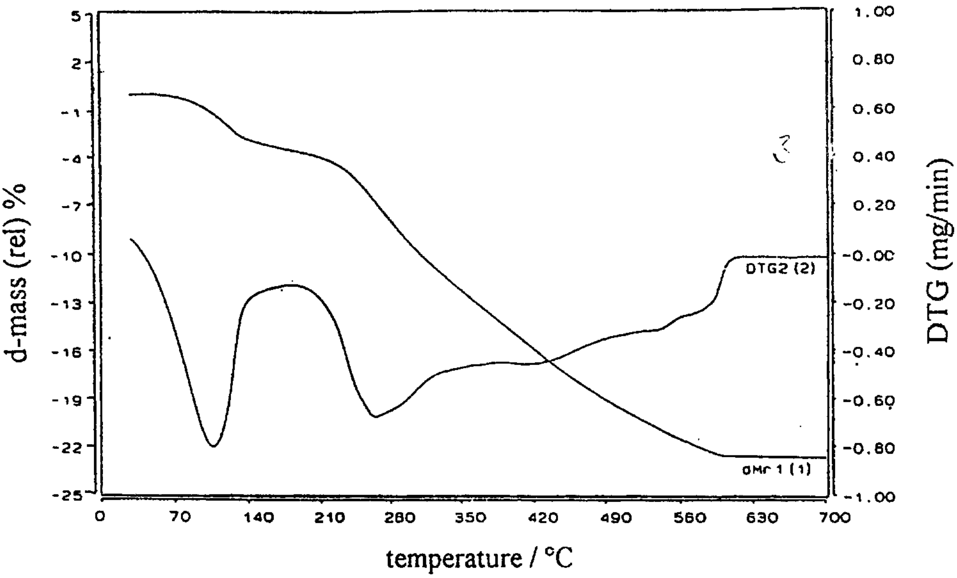

Fig. 3 TG and DTG curves of substrate V Z1

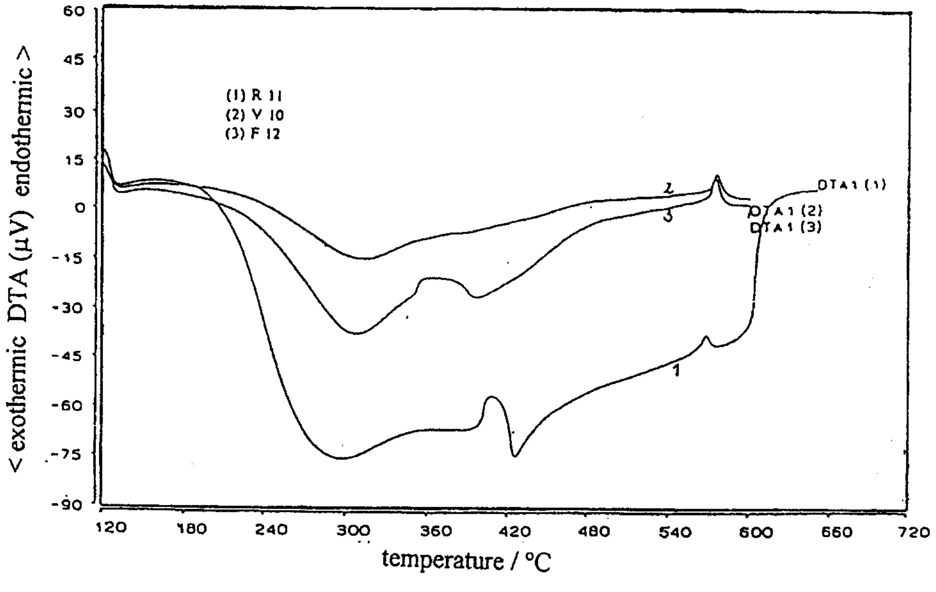

Fig. 4 DTA curves of different soil substrates

The DTA curves show two exothermic maxima in the temperature range 180–600°C (Fig. 4).

In accordance with [7], the two peak areas are given the names LER and HER (low exothermic reaction, high exothermic reaction). For sample R11 (in Fig. 5) the two peak areas are marked. As the DTA plots are given in ASCII

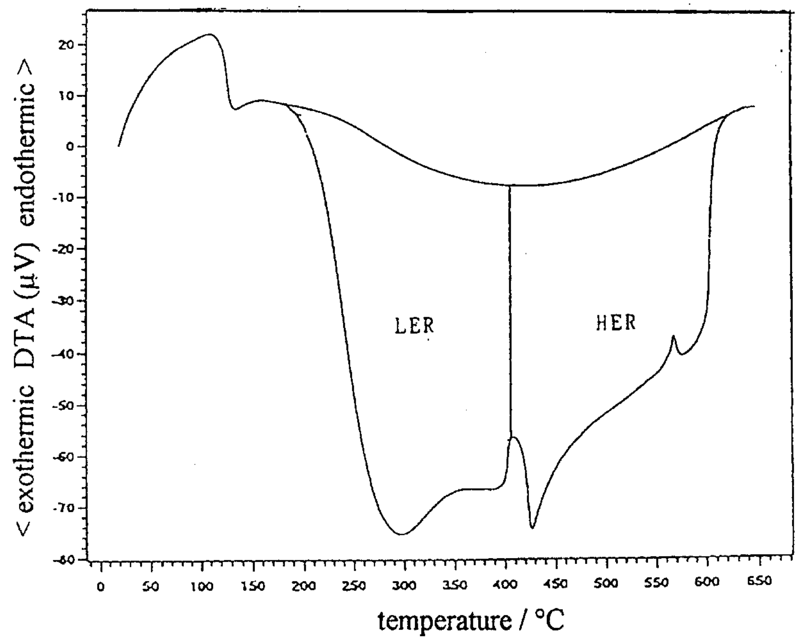

Fig. 5 LER and HER areas of R 11

files, the peak areas can easily be calculated by numerical quadrature (Simpon's rule) [8]. The areas represent the reaction enthalpies of mixtures of easily oxidizable organics (LER) and of organic compounds which are more difficult to oxidize (HER).

To show which of the two groups predominates in the combustion enthalpy of the OM in a given substrate the quotient Q is calculated.

$$Q = \frac{LER}{HER}$$

In Table 2 the reaction temperatures and the quotients Q are listed for the investigated substrates.

Reaction temperature

The reaction temperature is defined as the extrapolated initial temperature (the intersection point of the tangent and the baseline). This temperature is less dependent on the measurement conditions than the onset- and peak temperatures [9]. The substrate of the sewage pond (B 62) shows an extremely low reaction temperature. This effect is due to the large amount of semivolatile and weakly adsorbed organic materials on the mineral carrier. In the OM of the inflow substrates (R 11, R 13) the amount of these materials is significant as well.

Table 2 Results of the DTA measurements

Substrate	Reaction temperature/°C	*Q*
B 62	216.8	
V Z1	240.0	0.56
R 11	239.8	1.16
V 72	268.5	1.53
R 13	247.7	1.67
F 12	277.1	2.05
V 82	270.6	2.39
F 23	273.7	2.81
F 63	276.3	2.88
V 10	263.6	3.57
F 08	263.2	5.08
F 05	257.5	6.28

As expected, the lowland substrate (V Z1) also belongs to the first group with respect to its reaction temperature. Hemicelluloses and celluloses (O-alkylated structures) are responsible for the start of the oxidation at low temperatures. The relatively small organic molecules are products of the humification process [4, 1].

The remaining substrates hardly differ in their reaction temperatures. This is due to the low concentration or absence of easily oxidizable compounds. Temperatures of 300–350°C have been reported as peak temperature for the combustion of the OM of farm soil substrates [5]. The chemical nature of the oxidizable compounds cannot be clarified by thermal analysis only but pyrolysis field ionisation mass spectrometry revealed mono- and polysaccharides as main representatives of the organic matter in LER in soil substrates. Aromatic decomposition products of lignin, nitrogen compounds and long-chained alkanes/alkenes mainly contribute to HER. The HER components are cross-linked with each other and can be strongly associated with the mineral matrix [5]. In the OM of soil substrates weakly adsorbed and thermolabile substances, the typical humic skeleton and large macromolecular structures with high proportion of cross-linkage and the part of the humic skeleton which is strongly associated with the mineral matrix (organo-mineral complexes) are to be distinguished. In sand substrates or silty sand the proportion of organo-mineral complexes is very small [5, 7], and HER mainly originates from large macromolecular structures.

The DTA results obtained for artifical substrates (K 1, K 2, K 3) prove that the amount of OM has no significant influence on the reaction temperature if there are no differences in the composition of the OM and in the interaction between the OM and mineral carrier.

K 1: reaction temperature = 259.9°C
K 2: reaction temperature = 258.2°C
K 3: reaction temperature = 255.4°C

Ratio Q of reaction enthalpies

The substrates have low *Q* values if the HER area is large. Typical examples are the inflow substrates (R 11, R 13) as well as the lowland (moor) substrates. The LER area of these substrates which starts at low temperatures requires very large HER areas which represent the reaction enthalpies of single macromolecular structures of cross-linked aliphatic and aromatic organic compounds, as discussed earlier.

During humification, macromolecules are degraded while small easily oxidizable molecules can be incorporated in the humic skeleton. Plots 2 and 3 in Fig. 4 show that the proportion of the HER area in the closed sewage farm substrate becomes smaller. In the control sample this tendency sustains.

According to their *Q*-values the other substrates can be arranged in further two groups. One group covers a control sample with high content of litter (V 82), sewage farm substrates outside the inflow (F 23, F 63) and the inflow substrate of the recently closed sewage area (F 12). The *Q* values are between 2 and 3.

Compared with the first group of substrates ($Q<1.7$), the proportion of single macromolecular particles decreases. This degradation process continues in the third group of well aerated farmland substrates.

Substrate V 10 and also the sewage areas closed 20 years ago, F 08 and F 05, belong to group III ($Q<3$).

In these substrates the OM has further developed in the direction of a dynamic equilibrium according to its molecular structure. The two maxima of the LER and HER areas start to fuse (Fig. 4).

Control sample V 72 (green fallow) has an expected reaction temperature of about 270°C. The low *Q* value ($Q=1.53$) is based on the utilization and the OM content. Because of the utilization, organic substances with macromolecular structure (litter) are provided. In total, OM amounts to only 1.47%, the proportion of litter in the OM is high. Therefore HER predominates.

Conclusion

The organic matter in the inflow substrates of sewage areas was shown to contain a significant amount of volatile and ealisy oxidizable compounds. They are brought by suspended particles of the sewage.

Beside the small and volatile molecules some macromolecular particles predominate and are responsible for the immense heat release in the higher temperature range studied (HER).

In substrates from outside the inflows and from closed sewage farms the amount of volatile organic materials decreases rapidly. In their reaction temperatures these substrates hardly differ from control samples.

The proportion of macromolecules also decreases during the humification process. Further investigations are needed to clarify the different compositions of the organic matter in the different substrates (sewage pond, inflow, control sample) particularly with regard to volatile organic compounds being typical of sewage farms. The chemical fate of these compounds may be important for risk assessment.

References

1 L. Beyer, U. Irmler, U. Schleuss and C. Wachendorf, Mitteil. Dt. Bodenkundl. Gesell., 71 (1993) 287.
2 K. Grunewald, Z. Pflanzenernähr. Bodenk., 157 (1994) 125.
3 K. Grunewald and W. Bechmann, Zschr. Terra Tech., 3 (1994) 28.
4 R. Hempfling, F. Ziegler, W. Zech and H.-R. Schulten, Z. Pflanzenernähr. Bodenk., 150 (1987) 179.
5 P. Leinweber, H.-R. Schulten and C. Horte, Thermochim. Acta, 194 (1992) 175.
6 T. Satoh, Soil Sci. Plant Nutr., 30 (1984) 1.
7 T. Satoh, Soil Sci. Plant Nutr., 30 (1984) 95.
8 W. H. Press, S. A. Teukolsky, T. Vetterling and B. P. Flannery, Numerical Recipes in Fortran, second edition, Cambridge University Press 1992, p. 124.
9 H. G. Mc Adie, P. D. Garn and O. Menis, Standard Reference Materials: Selection of Differential Thermal Analysis Temperature Standards Through a Comparative Study, NBS Special Publication 1972, p. 260.